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EFFECT OF THE PLASTICIZER ON STRUCTURE FORMATION IN PORIFIED POLYDISPERSED GLASS CERAMIC COMPOSITES

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A composite material based on synthetic phosphates strengthened with 50 wt.% glass phase has been obtained. The porosity of the material is 48 – 61%, depending on the plasticizer agent and sintering regime. The experimental samples showed adequate mechanical strength and biochemical solubility, which commends this material for use as a biomaterial.

The composite ceramic based on hydroxyapatite (HAp) $\text{Ca}_{10-x}(\text{PO}_4)_6(\text{OH})_2$ possesses a number of unique properties, as a result of which it has found wide applications in engineering, biotechnologies, and other fields [1]. Other calcium phosphates have quite wide applications in medicine. Examples are different modifications of tri- and tetracalcium phosphates and their solid solutions with HAp [1, 2].

Medicine and other fields now require materials with a diverse spectrum of useful properties, which depend on their chemical composition and on the crystalline and morphological structures. The most effective method of imparting new properties to most materials remains changing their morphological structure by regulating the sizes of the micro- and macropores. This pertains, first and foremost, to materials which have a cellular structure and high porosity and are based on silicates and other refractory nonmetallic compounds.

Materials based on HAp and silicate-borate-sodium glasses possess a complicated grain and porous structure [3]. The strength of the structures of such materials largely depends on the method of formation and the physical-chemical properties of their components.

Different types of heterogeneous microsystems play a special role in the formation of the structures of high-porosity composite materials. Examples of such systems are suspensions (solid : liquid), foams (gas : liquid), and powders (solid : gas).

Materials with definite prescribed density and strength are produced by ceramic technology. The principal technological methods are considered to be the stages of successive consolidation of solid-phase particles with a transition from a

state of isolation into a compact state (densification and, less often, dedensification or porification) [4]. On the other hand they can be regarded as processes that change the type of bonds in three-dimensional structures from point contacts and coagulation bonds to extensive intergrowth along interphase and intercrystalline boundaries, accompanied by an increase of strength. Ordinarily, such processes largely depend on the degree of to which the volume of the system is filled with solid phases and on the granulometric composition of these phases, which is important to achieve already at the stage where the initial powders, suspensions, and slips are obtained as well as during the formation of these systems.

The present work examines glass ceramic compositions (GCC), based on calcium phosphates and a glass phase, and the technological methods of porifying and sintering them to study and optimize the combined effect of these factors on obtaining high-porosity structures with improved strength and biochemical properties. The interaction of heterogeneous calcium phosphate based microsystems, which are obtained by the sol-gel technology without using any special methods of deagglomeration of the batch components of the glass phase introduced into the composite materials to increase strength and bioconductivity, and two types of porifiers that volatilize during sintering are studied.

The GCC were prepared by sintering the phosphates with the components of the glass batch. The phosphates were synthesized by chemical precipitation in an alkaline medium using as reagents solutions of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)\text{H}_2\text{PO}_4$ with concentration 1 mole/liter in a definite ratio calculated according to the stoichiometric formula for HAp [1]. The precipitated gel was dried at $70 \pm 5^\circ\text{C}$ and then calcined in air in an electric muffle furnace at 800°C (1 h). After

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TABLE 1.

Sample	Plasticizing agent	Sintering temperature, °C	Parameter of GCC compacts							
			surface area, $\pm 0.01 \text{ cm}^2$	ratio $S_{\text{base}} : S_{\text{surf}}$	volume, cm^3	specific surface area, cm^2/cm^3	apparent density, g/cm^3	micro-porosity, %	macro-porosity, %	total computed porosity, %
GCC1	H ₂ O ₂	≤ 800 (stage I)*	6.42	0.580	1.032	6.20	1.463	21.7	27.2	48.9
GCC2	PVA	≤ 800 (stage I)*	6.90	0.541	1.223	5.65	1.218	52.4	9.2	61.6
GCC3**	PVA	≤ 800 (stage II)*	6.48	0.575	1.037	6.24	1.576	39.3	11.7	51.0

* The pressed sample was calcined.

** The unpressed powder calcined at 1100°C at the first stage.

heat-treatment the agglomerated calcium phosphate material was ground to particle sizes $\leq 160 \mu\text{m}$.

x-ray phase analysis showed that the material obtained contains a mixture of phosphates: HAp (the predominant phase), low-temperature tricalcium phosphate β -TCP (no more than 10%²), and a comparatively small amount ($< 2\%$) of phases of the type tetracalcium phosphate and calcium orthophosphate.

Glass containing oxides of silicon, sodium, boron, and other elements was used to prepare the GCC. The chemical composition of the batch was as follows (%): 33.00 SiO₂, 4.75 B₂O₃, 2.50 CaO, 1.00 MgO, 7.75 Na₂O, 1.00 K₂O, 50.00 calcium phosphates. The temperature range corresponding to the viscofluid state of the glass phase for the batch is 650 – 780°C.

The GCC was sintered in one or two stages. Samples of the composites GCC1 and GCC2 containing 50% glass phase were obtained by one-stage sintering at temperature $\leq 800^\circ\text{C}$. To make GCC3 samples with the same amount of glass the sintering was done in two stages with temperature 1100°C for the first sintering of the powder. The sintered material was ground to particle-size no greater than 160 μm and then pressed under pressure 30 – 35 MPa into 1.5 cm in diameter pellets and calcined at temperature $\leq 800^\circ\text{C}$.

It should be noted that all powders which were used in the composite batch and whose granulometric composition was checked consist of agglomerates of micrograins no larger than 160 μm . This ensures that composites with a fine-grain solid-phase texture and high strength will subsequently be obtained [1, 2].

Dry polyvinyl alcohol (PVA) in amounts 10% (above 100% of the GCC batch mass) and no more than 20% (above 100%) of a 30% solution of hydrogen peroxide were used as plasticizers for the batch powders to obtain a pressed powder with relative moisture content 12 – 14%. The sample sizes were measured immediately after pressing and at the end of sintering. When necessary the surfaces of the samples obtained were ground to give the samples a strict geometric shape.

The geometric parameters of the compacts are given in Table 1. The following equations were used calculate the micro- and macroporosities of the compacts:

$$\Pi_{\text{micro}} = 1 - \frac{P(1-B)}{\left(V - \frac{BP}{\gamma_{\text{fill}}}\right)\gamma};$$

$$\Pi_{\text{macro}} = 1 - \frac{P(1-B)}{V\gamma(1-\Pi_{\text{micro}})},$$

where Π_{micro} and Π_{macro} are the micro- and macroporosities, respectively, fractional units; P is the mass of a compact with a filler (plasticizer), g; B is the mass fraction of the plasticizer; V is the volume of the compact, cm^3 ; and, γ_{fill} and γ are, respectively, the densities of the filler and material, g/cm^3 .

The total porosity of the GCC samples was calculated using the apparent and pycnometric density according to the following formula:

$$\Pi = \left(1 - \frac{\rho_a}{\rho_t}\right) \times 100,$$

where ρ_a and ρ_t are the apparent and true densities respectively, g/cm^3 .

The mass losses of the composites obtained after the materials were immersed in a physiological solution for 2 and 5 days at 37 – 38°C — experiments *in vitro* — were determined to estimate the biosolubility of the composites obtained.

Using dry and half-dry compacts at relatively low molding pressure with two types of plasticizers makes it possible to follow the changes in the structural-rheological model of the GCC formed and the transition from a elastoviscous state of the powder components (Maxwellian model) to the viscoplastic state (Bingham model) [6].

Comparing the apparent density of the GCC1 and GCC2 samples showed that it depends on the plasticizing agent chosen (see Table 1). The higher apparent density of the GCC3 compacts as compared with the GCC2 compacts can be explained by the fact that the batch used for GCC3 contains, before the final sintering, not individual components of

² Mass content, here and below.

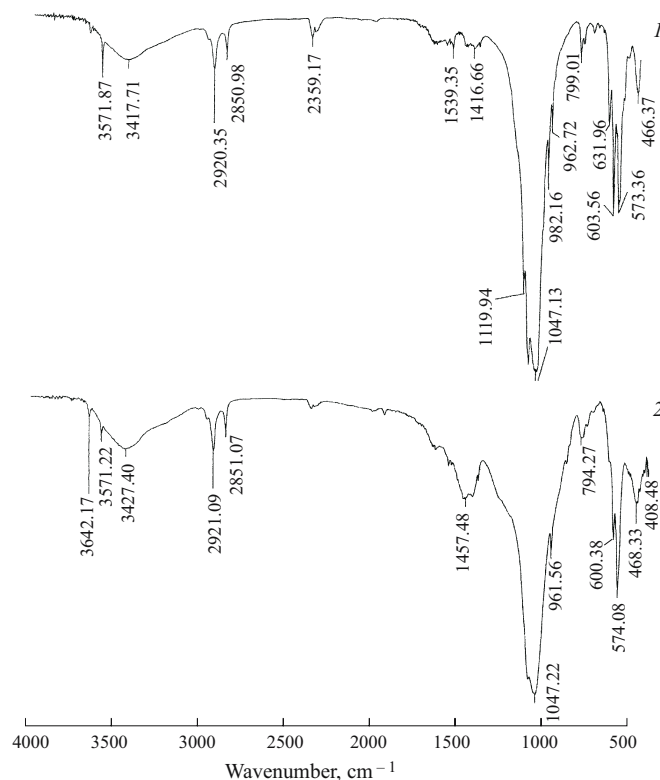


Fig. 1. IR absorption of the initial calcium phosphate (1) and the GCC1 composite (2).

glass but rather a finished glass phase which is formed during sintering at 1100°C.

The technological problem of producing samples of composites was solved by reaching a pseudoplastic solid-like state [4, 6] of heterogeneous microsystems (calcium phosphate + glass components + plasticizing agent). This state is obtained by molding samples by ordinary unilateral compression under low pressure.

It was established that when H_2O_2 is used as the porifier the GCC1 compacts are characterized by close values of the micro- and macroporosities (see Table 1). Used when pressing a GCC2 batch PVA increases the microporosity relative to the macroporosity. This can be explained by the fact that when samples are pressed with dry PVA the particles of PVA fill the pores in the granules themselves and in agglomerates of grains of the components of the GCC2 batch, thereby decreasing the macroporosity fraction. This is confirmed by the fact that the degree of moldability of a GCC2 compact with PVA, as estimated from the area ratio $S_{base} : S_{surf}$ (S_{surf} is the surface area of a cylindrical sample and S_{base} is the area of the base of the cylinder), is lowest among GCC2 samples.

Moistening GCC1 powder molds with hydrogen peroxide results in some nonuniformity in the density of the compacts, which is not completely removed at low pressing pressures and can lead to a high macroporosity. When a GCC2 batch with PVA is pressed it is densified because the smaller particles of the batch components and the plasticizer are redistributed in the pore space of the agglomerates of the

TABLE 2.

Change in the parameters	Sample		
	GCC1	GCC2	GCC3
Volume, $\Delta V/V_0$, %	0.30 – 0.35	0.50 – 0.80	3.30 – 3.80
Height, $\Delta h/h_0$, %	0.4 – 0.5	0.6 – 1.1	3.5 – 4.2
Diameter, $\Delta d/d_0$, %	0.05 – 0.08	0.10 – 0.15	0.12 – 0.18
Anisotropy factor ($\Delta h/h_0$)/($\Delta d/d_0$)	6.5 – 8.0	6.0 – 7.5	23.0 – 25.0
Mass $\Delta m/m_0$, %	12.5	18.1	17.4
Density $\Delta \rho_c/\rho_0$, %	12.3	17.9	12.8

grains of the same components. In our opinion, such a redistribution results in micropores being formed predominately.

The lower microporosity fraction in GCC3 samples as compared with GCC2 samples is due to a decrease of the total porosity of the pressed material as a result of it being used after the preliminary stage of sintering.

The macro- and microstructures of high-porosity poly-dispersed systems form during sintering of molded samples. The change in the parameters of GCC samples after the final sintering is reflected in Table 2. The formation of a macrostructure in the samples depends on the choice of plasticizer and the temperature of the first sintering, as is evident for the anisotropy factor for the GCC2 and GCC3 samples. In the case of one-stage sintering of GCC at temperature $\leq 800^\circ\text{C}$ an amorphous glass phase forms in parallel and interacts with the polycrystalline phosphate grains, and pores are formed as a result of volatilizing of the plasticizer and the gaseous products of decomposition of the batch.

It is convenient to view the microstructure of the composites obtained as an amorphous matrix into which polycrystalline phosphate grains are incorporated. The fact that the x-ray diffraction patterns of the initial phosphates and the sintered composites are alike serves to confirm such a morphological structure of the materials which we have developed. The presence of wide absorption bands characteristic for Si – O bonds in the IR spectrum of the composites attests to the amorphous character of the glass “matrix.” These bands lie in the same spectral interval as the absorption band near 1090 cm^{-1} , characteristic for one of the types of vibrations of the complexes $[\text{PO}_4]^{3-}$ (see Fig. 1).

The IR absorption spectrum of the GCC1 composite is characteristic for all of the composite materials which we studied. The absorption bands near 465, 573, 602, 962, 1047, and 1090 cm^{-1} , associated with the vibrations of the complexes $[\text{PO}_4]^{3-}$, are completely reproduced in the IR spectra of all of the compounds studied with the exception of the GCC3 samples. A $2 - 9\text{ cm}^{-1}$ shift of the main absorption bands is observed in the spectra of these compounds. In addition, the absorption bands near 632 cm^{-1} are essentially absent in these samples and in the GCC1 and GCC2 composites; this can be explained by the very low intensity of the low-energy vibrations of the $[\text{OH}]^-$ complexes. However, the

high-energy vibrations of $[\text{OH}]^-$ near 3572 cm^{-1} are clearly seen in all IR spectra. The presence of the $[\text{OH}]^-$ complexes in the synthesized materials confirms the presence of HAp as the predominant crystalline component.

Appreciable absorption bands are observed in the intervals $1400 - 1550$ and $2800 - 3100\text{ cm}^{-1}$ in the IR spectra presented. They could be due to the vibrations of the N – H and C – O bands. In reality, nitrogen and carbon compounds could be present in the materials as residual impurities after heat-treatment. The compounds of the same elements can be present in the surface layers of the finished samples as a result of being absorbed from air.

Thus, the composites GCC1 and GCC2 are obtained as a result of solid-liquid-phase sintering, and a characteristic liquid-phase sintering should occur during the synthesis of the GCC3 samples. This type of sintering is based on melting of the glass phase at temperatures $\leq 800^\circ\text{C}$, which occurs in parallel with the densification of the GCC3 compacts [3, 7].

The high porosity and the corresponding strength of the structure of the composites are due to the formation of a reticular-cellular framework of the potassium-sodium-calcium-borosilicate glass matrix in which crystalline phosphate micrograins with their own intrinsic porosity and pores, appearing as a result of gas formation during heat-treatment, are distributed. The sizes and number of pores depend on the type of pore producer and on the number of sintering stages, during which water vapor and carbon oxides volatilize as a result of the decomposition of sodium carbonate and boric acid which are components of the batch of the glass phase [7, 8].

PVA powder used as a plasticizer gives higher porosity than liquid H_2O_2 . However, for the GCC3 samples obtained by sintering in two stages using PVA to form them before the final sintering a lower porosity than for the GCC2 composites is characteristic (Table 3). During GCC3 synthesis the indicated batch components decompose even at the first stage of sintering at 1100°C . When compacts with PVA are sintered at temperature $\leq 800^\circ\text{C}$ the PVA particles are burned out in parallel with the compacts densified predominantly in the radial direction and gases driven off in the vertical direction [8], which gives rise to a large anisotropy of the densification of the GCC3 samples during the final sintering (see Table 2). It should be noted that the total computed porosities of the GCC compacts are comparable to the total porosities of the sintered samples of the composites (See Tables 1 and 3).

Similar samples of the high-porosity biogenic HAp – glass components were obtained and investigated under the same technological conditions of one-stage sintering using PVA as the plasticizer. The total porosity of the samples reached about 58%, whence it follows that the mechanism of sintering of these composites is essentially independent of the origin of the phosphate chosen and is determined by the type of plasticizer and the sintering regime.

The values of the mechanical strength of the GCC1 and GCC2 samples agree with one another and with the porosity

TABLE 3.

Sample	Density, g/cm^3		Total porosity, %	Compression strength, MPa	Mass losses, $10^{-4}\text{ g}/(\text{cm}^2 \cdot \text{day})$	
	apparent	pycnometric			after 2 days	after 5 days
GCC1	1.28	2.48	48	42	9.3	9.5
GCC2	0.99	2.56	61	6	3.4	10.7
GCC3	1.37	2.64*	49	37	14.8	–

* Calculated using the formula for the additive density of multi-component glasses and ceramics [9].

(65 – 80%) and compression strength, which is 3 – 5 MPa for the Synthacer biomaterial [2]. This material is obtained by pressing a fine HAp powder with granules of a volatile porifier, which leave behind pores up to $600\text{ }\mu\text{m}$ in size. In the biomaterials which we obtained and investigated biogenic HAp – glass with close composition and the same sintering temperature, the pore sizes usually lie in the range $1 - 300\text{ }\mu\text{m}$ [7]. It should be expected that the pore-size distribution also falls within close limits in the GCC samples studied in the present work.

The mass losses of the samples after immersion in a physiological solution at 37°C (*in vitro* tests) are of interest. The test results, which are presented in Table 3, show that the GCC3 composites which in a solution for 2 days have better biosolubility with mechanical strength comparable to that of spongy bones [7].

The adequate mechanical strength and biochemical solubility of the experimental samples commend these materials for use as biomaterials in practical applications.

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